# Synthesis and Characterisation of Layered Hydroxy Anion Exchange Materials

## Abstract

This thesis concerns the synthesis and characterisation of layered hydroxy anion exchange materials. The incorporation of rare-earth cations into these materials offers the potential to combine the optical, magnetic and catalytic properties of the lanthanides with the flexibility of intercalation hosts.

A review of the literature surrounding intercalation chemistry and materials is presented in **Chapter 1**. Here the synthesis, structure and anion exchange reactions of layered hydroxides and their applications in the fields of catalysis, separation science, polymer additives and biological storage and delivery are discussed.

**Chapter 2** describes the hydrothermal synthesis and anion exchange capacity of new anion exchange host lattices containing the smaller lanthanide cations, with the composition $Ln_2(OH)_5NO_3\cdot1.5H_2O$ (Ln = Y, Gd - Lu), with Gd marking a limiting cation radius. Anion exchange reactions are facile with a wide range of organic carboxylates and sulfonates and investigations into their selectivity and optical properties have been carried out. This family has also been expanded to include $Ln_2(OH)_5X\cdot1.5H_2O$ (X = Cl, Br; Ln = Y, Dy, Er, Yb) and crystal structures for orthorhombic and monoclinic $Yb_2(OH)_5Cl\cdot1.5H_2O$ are reported.

The findings of a time-resolved *in situ* X-ray powder diffraction study form the basis of **Chapter 3**. Three different phases with the layer composition $[Yb_2(OH)_5]^+$; $Yb_2(OH)_5NO_3\cdot1.5H_2O$ d = 9.2 Å (1), $Yb_2(OH)_5NO_3\cdot2H_2O$ d = 9.4 Å (2) and $Yb_2(OH)_5NO_3\cdot H_2O$ d = 8.5 Å (3) were observed and shown to ultimately transform to a 3D structure $Yb_4O(OH)_9NO_3$ d = 8.0 Å (4). Single crystal structures are given for phases 2 and 3, and the structure of 4 has been refined. The effects of temperature and metal concentration on phase formation have been investigated and compared with *ex situ* results. A full kinetic analysis is presented including the activation energy for the formation of phase 2. The values extracted indicate that the mechanism of crystallisation is phase boundary controlled.

In **Chapter 4** the room temperature precipitation synthesis of a related family of anion exchange host lattices with the composition, $Ln_2(OH)_5NO_3\cdot H_2O$ (Ln = Y, Eu–Er) and MgAl layered double hydroxides incorporating the precious metals Ru and Pd are discussed.

Details of synthetic routes to the novel materials described and the methods of characterisation used are given in **Chapter 5**.

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# Abbreviations

| | |
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| AQDS | 2,6-Anthraquinonedisulfonate |
| BDA | Benzenedicarboxylate |
| EDS | Energy-dispersive X-ray spectroscopy |
| EDXRD | Energy-dispersive X-ray diffraction |
| FTIR | Fourier transform infra-red |
| HDS | Hydroxy double salt |
| LDH | Layered double hydroxide |
| LRH | Layered rare earth hydroxide |
| NDS | 2,6-Naphthalenedisulfonate |
| NMR | Nuclear magnetic resonance |
| NZA | Zinc nickel hydroxy acetate |
| SAED | Selected area electron diffraction |
| TEM | Transmission electron microscopy |
| TGA | Thermogravimetric analysis |
| UV | Ultra-violet |
| XRD | X-ray diffraction |
| ZCA | Zinc copper hydroxy acetate |
| ZHA | Zinc hydroxy acetate |

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